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NUCLEATION OF VOIDS

Final Report

(covering the entire period of the contract)

October 1, 1971 - January 31, 1977

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ABSTRACT

The objective of this contract was the successful prediction of the conditions under which nucleation occurs in metals, as a result of the high concentrations of vacancies and interstitial atoms (and gas atoms) present in reactor environments. This has been accomplished by 1) Generalizing homogeneous nucleation theory to account for nucleation of matter (i.e. vacancies) in the presence of its antimatter (i.e. interstitials). 2) Further generalizing the theory to account for the effects of both trapped and soluble gas. 3) Modifying the theory to describe interstitial loop formation and including the effects of external stress.

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The discovery in 1967 by Cawthorn and Fulton¹ that voids in materials during exposure to fast neutrons soon led to major research efforts since it was almost immediately realized that such void formation would cause warping and swelling of structural components in reactor cores. While some progress was made on the experimental front, interpretation was difficult for the following reasons: 1) reactors were difficult to instrument so the temperatures and fluxes to which the samples were actually exposed were quite uncertain. 2) While well characterized experiments could be and were performed using accelerators, extrapolation of experiments at these displacement rates to the reactor range was very uncertain since the underlying theory was so poorly understood. Attempts were made to apply homogeneous nucleation theory to this problem by viewing the vacancies as equivalent to atoms and the voids, i.e. vacancy clusters as the nuclei. This did not work! The difficulty was that in materials under irradiation there are also present, in concentrations much higher than equilibrium concentrations, the anti-matter of vacancies, i.e. interstitial atoms. An interstitial, on combining with a vacancy cluster, makes it smaller and thus hinders nucleation. Looking at the problem from this viewpoint makes it obvious that if vacancies and interstitials arrive at vacancy clusters at the same rate, no nucleation is possible, no matter how high one makes the vacancy supersaturation. Another difficulty with the theory was that it was becoming apparent from the experiments that gases, helium in particular, were playing a crucial role in the reactor results, but that this was not always the case in the accelerator experiments. It was the resolution of these difficulties, i.e. the development of a valid theory for the nucleation of voids, both in the absence and in the presence of gases (soluble, insoluble and also of the kind which dissociate or form by chemical reaction, e.g. H_2 , H_2O , CH_4 etc.), which was the goal of this contract.

Since the beginning of this grant, we (Dr. Hartmut Wiedersich, Materials Science Division, Argonne National Laboratory and myself) have been able to:

1) show how to generalize nucleation theory to correctly account for the anti-nucleating effect of interstitial atoms on void nucleation and make sample calculations using properties typical of those of nickel² 2) show how to account for the nucleating effect of insoluble gas when the rate of arrival of vacancies and interstitials at a gas vacancy cluster is much larger than the rate of arrival (and of loss) of gas molecules³, and make sample calculations using the properties of nickel⁴ 3) show how to account for the nucleating effect of supersaturated gas when the gas can enter and leave the vacancy cluster so readily that it is in equilibrium with the gas interstitially in the lattice⁵ (this last study also involved Dr. J.J. Burton, now at Exxon Corporate Research Laboratories). All of these studies were cases where the standard ideas of nucleation theory could not be used directly because of the existence of the anti-matter to the nucleating species, i.e. the interstitial atoms.

We have also discovered a much clearer way of deriving nucleation theory; a way which not only makes our derivation for void and interstitial nucleation clearer, but also helps for ordinary nucleation theory. We have written a paper⁶ and two review articles^{7,8} on void nucleation in which this approach is central. In it we show that the emission rate of vacancies (or interstitials) from a defect cluster can be related to the concentrations of such clusters in a metal at equilibrium.

This new approach has been quite fruitful. We have used it to study chemical nucleation, e.g. the nucleation of protons to form H₂ filled voids. We were able to establish that if the equilibrium between the H₂ molecules in the void and the protons in the lattice is very rapid (more rapid than the arrival and emission

of vacancies and interstitials) that there is no nucleation effect due to protons (except via changes in the surface free energy).

If the reaction rate is rapid, but the vacancies are much more mobile than the protons, then the rate of nucleation is indeed affected. One has to generalize La Place's equation (which describes the relation between the pressure inside a bubble and its radius) to account for the dynamic effect of rapid vacancy arrival. This we have done. However, we still need to include the effects of interstitial to make this theory complete. We have also examined the effects of external stress in the presence of both vacancies and interstitials (but with no gas present) and obtained quantitative expressions for the thus modified rate of nucleation.

At the time (January 1976) of the last renewal of this contract, because I would be on sabbatical leave from September 1976 to August 1977 and thus, by ERDA policy (except on my own time) unable to work on this contract, it was decided to make this renewal be a final extension. Unfortunately, the problems posed by the simultaneous effects of stress and vacancies proved to be quite difficult. In fact, it wasn't until October 1976 that we solved that problem and no time remained to include the interstitials. We also succeeded in establishing the framework for considering the different types of nucleation that occur depending on whether the chemical reaction rates are fast or slow compared to the vacancy and interstitial arrival rates and including the simultaneous effects of stress but could not complete the derivations.

Nonetheless, this contract has met most of its goals. We have provided a theory which accounts for simultaneous effects of vacancies, interstitials, and both mobile and immobile gas atoms. This theory has shown that at very high displacement rates the gas becomes unimportant but that at lower displacement rates it dominates the nucleation. It thus qualitatively accounts for the

observed differences in accelerator and reactor results. While some of the parameters needed are somewhat uncertain, it nevertheless provides a reliable method for extrapolating experimental results obtained in one range of conditions to quite different conditions, even when, as in the example of reactors vs. accelerators, the very mechanism involved changes. We have written an extensive review article (it also includes some new material) which (in slightly different forms) we are publishing in two different places^{8,10} to insure adequate attention by the scientific and engineering community.

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8. H. Wiedersich and J.L. Katz, "The Nucleation of Voids and Other Irradiation-Produced Defect Aggregates," published in the *Proceedings of the Workshop on Correlation of Neutron and Charged Particle Damage* held at Oak Ridge National Laboratory, June 8-10, 1976, CONF-760623; also submitted as ERDA report C00-2183-10.

LIST OF PUBLICATIONS RESULTING FROM THE CONTRACT

No separate list is provided since references 2 to 8 in the References above comprise them all.